Introduction to Crystallography, 결정학개론 (445.206.001)

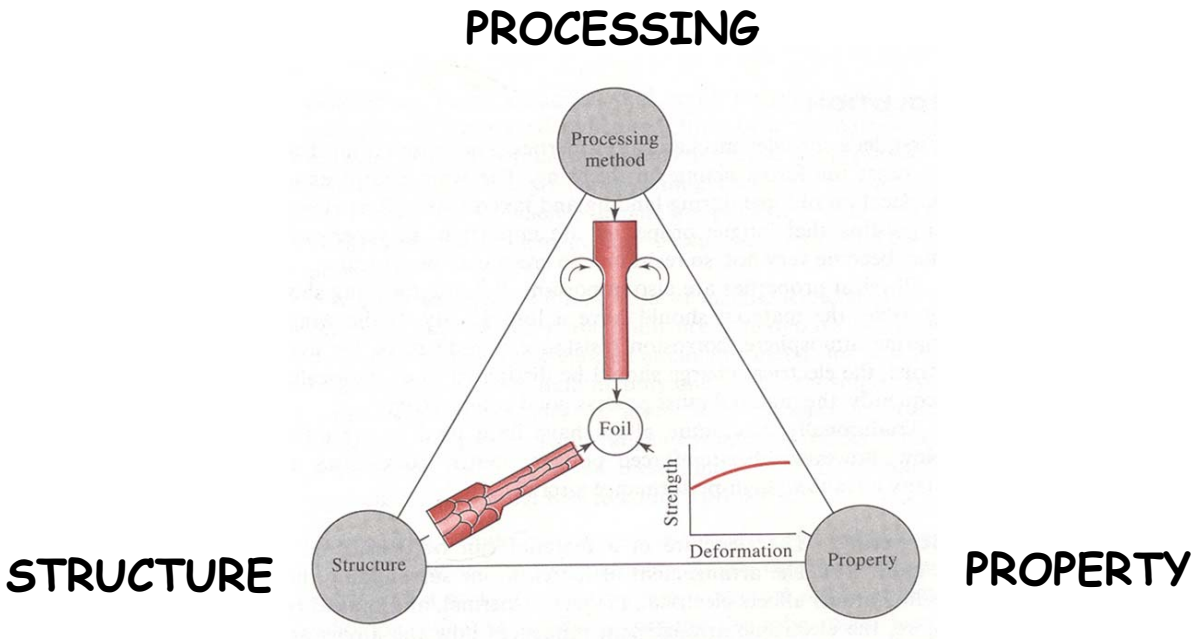
- **Crystal**
  - ✓ An anisotropic, homogeneous body consisting of a **3-dimensional periodic ordering** of atoms, ions, or molecules
  - ✓ Solids which possess **long-range, 3-dimensional molecular order**

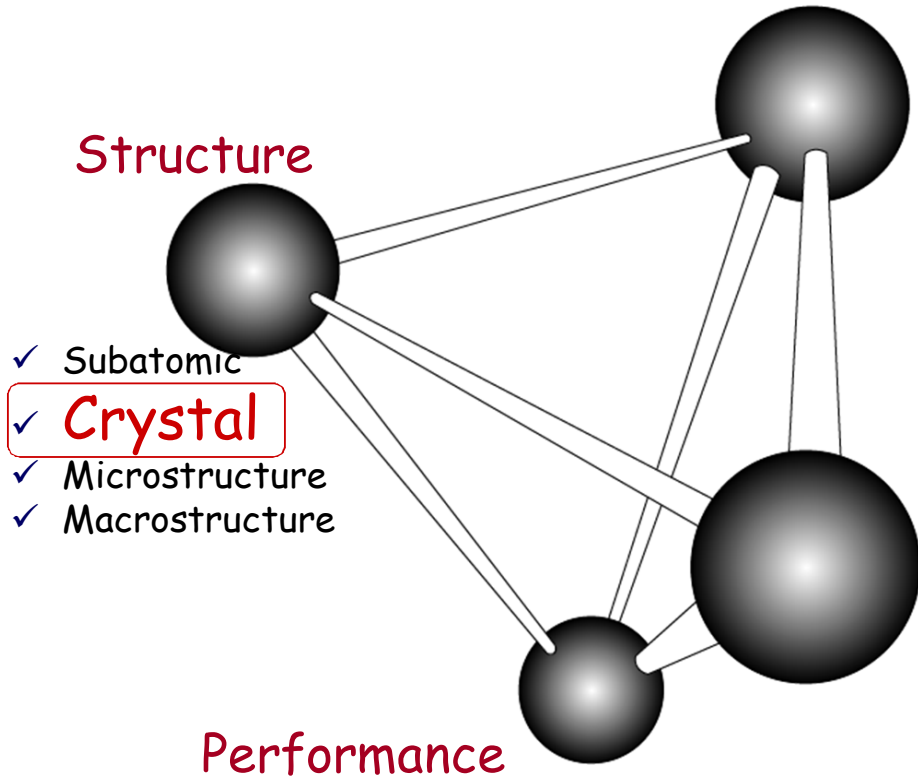
- **Crystallography** – concerned with the laws governing the **crystalline state** of solid materials with the arrangement of atoms (molecules, ions) in crystals and with their physical and chemical properties, their synthesis and their growth. (Ott)
  - ✓ 결정 구조와 이 구조에 기인하는 화학적, 물리적 성질을 연구하는 학문

- Perfect crystal vs. Crystals with defects

Materials Science & Engineering

- Relation between STRUCTURE, PROPERTY & PROCESSING





Structure

- ✓ Subatomic
- ✓ Crystal
- ✓ Microstructure
- ✓ Macrostructure

Processing

- ✓ Sintering
- ✓ Heat treatment
- ✓ Thin Film
- ✓ Melt process
- ✓ Mechanical

Properties

- ✓ Mechanical
- ✓ Electrical
- ✓ Magnetic
- ✓ Thermal
- ✓ Optical

Performance

Retention of shape ↓ ↓ Retention of volume

Representation of the state	Retention of shape	Retention of volume	Distribution of molecules	Physical properties
a) Gas (gas)	No	No	Statistically homo-geneous[1]	Isotropic[2]
b) Liquid (liquid)	Yes	No		
c) Crystal (crystal)	Yes	Yes	Periodically homo-geneous[1]	Anisotropic[3]

Physical properties

Schematic representation of the states of matter

??? → See the Ott book

[1] Equal physical properties in parallel directions ⟹
[2] Equal physical properties in all directions
[3] Different physical properties in different directions

Not "solid"

"Crystal" vs. "Solid"

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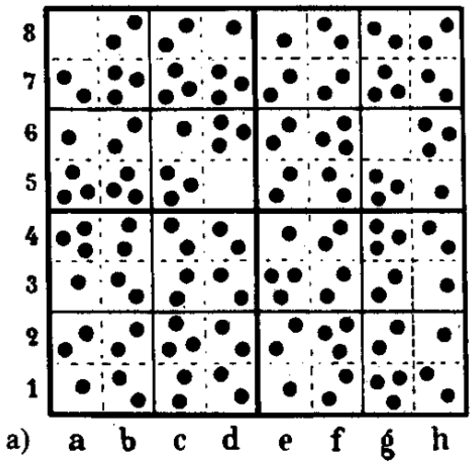
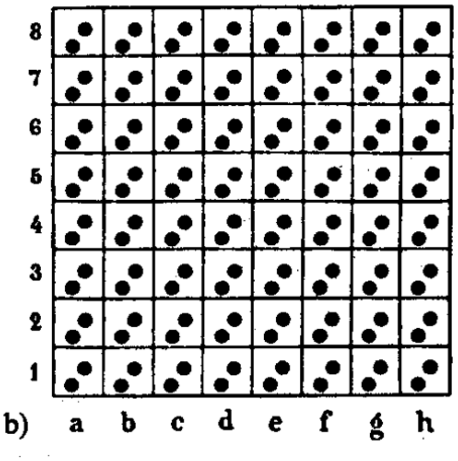
Homogeneity





Statistical homogeneity

: the same behavior in parallel directions → **isotropic** properties

Periodic homogeneity

: different behavior in different directions → **anisotropic** properties

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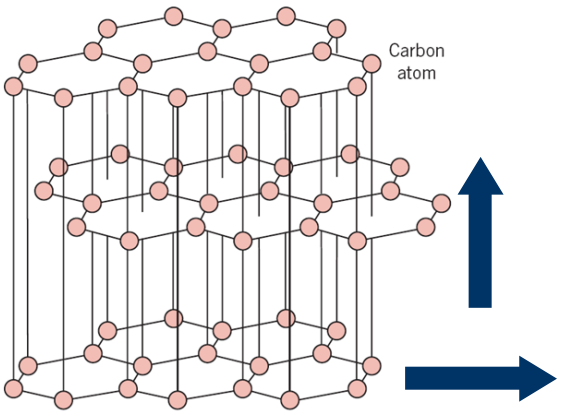
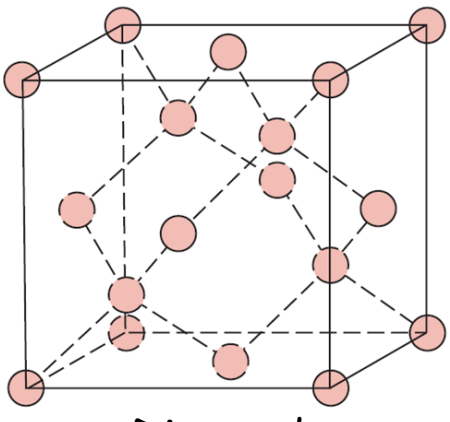
Anisotropy in electrical properties

- Electrical conductivity
  - ✓ Graphite is anisotropic with respect to electrical conductivity
- Dielectric constant



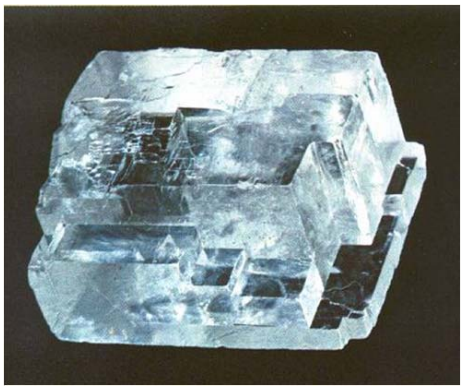
Graphite



Diamond

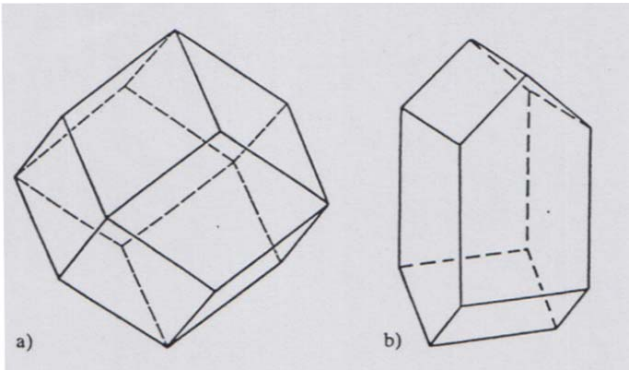
Anisotropy in mechanical properties

- Cleavage(벽개) - flat surfaces parallel to crystallographic planes
  - ✓ Fracture in glass - irregularly shaped pieces



Rhombohedral cleavage of calcite (CaCO3)

rhombo-dodecahedron



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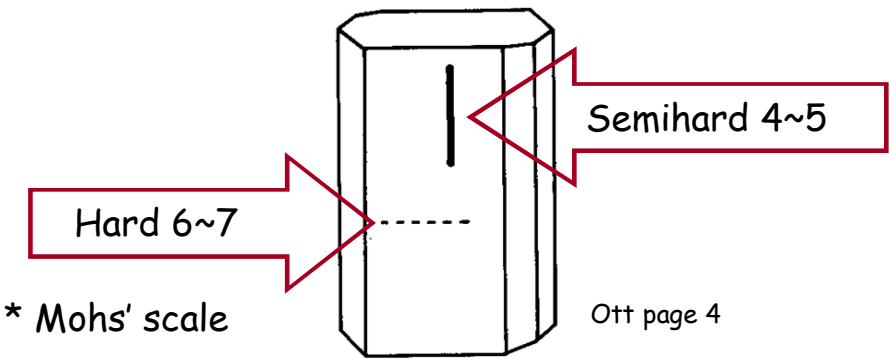
Vitamin B_{12}

Anisotropy in mechanical properties

- Different deformation in different directions
- Hardness (경도) - resistance to external stresses in one direction (scratching), in two directions (abrasion), and in three directions (penetration)



* Mohs' scale

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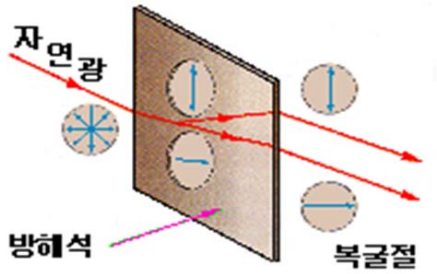
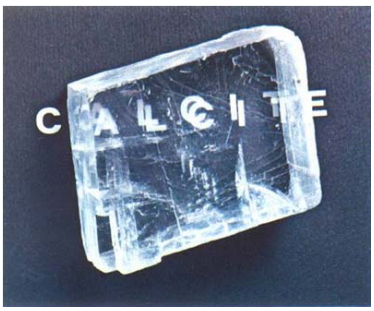
The hardness of kyanite(Al_2OSiO_4) is different in the two directions

Anisotropy in optical properties

- Birefringence (복굴절) - formation of two polarized light waves traveling in different directions, i.e. production of two rays of polarized light
  - ✓ ex) calcite ($CaCO_3$)

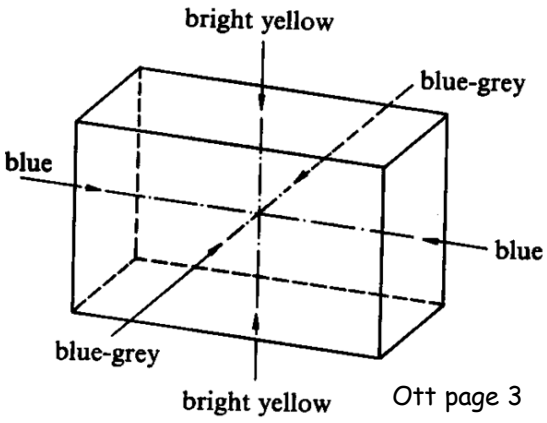


extraordinary ray
ordinary ray



Anisotropy in optical properties

- Pleochroism (다색성) - display more than one color due to the different absorption of light in different directions (dichroism, trichroism)



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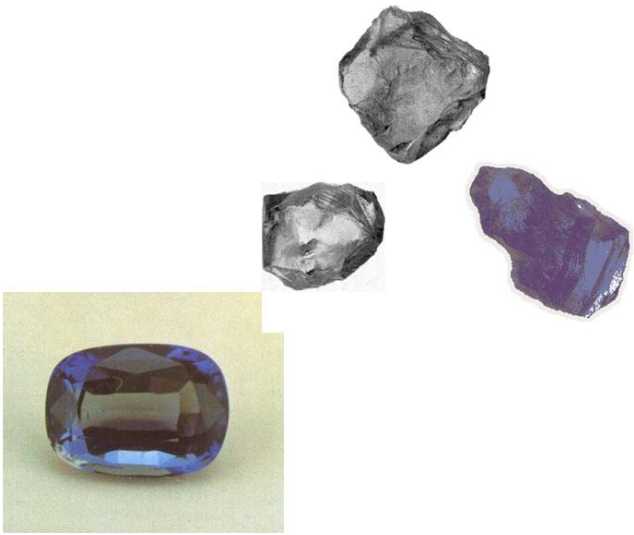
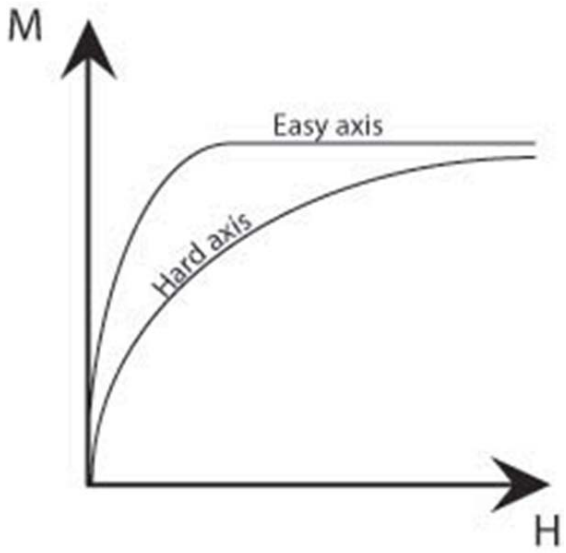
cordierite ($Mg_2Al_4Si_5O_8$)
orthorhombic



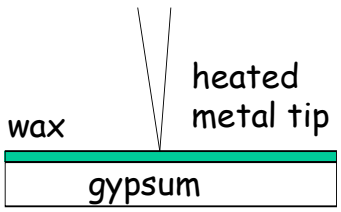
Anisotropy in magnetic properties

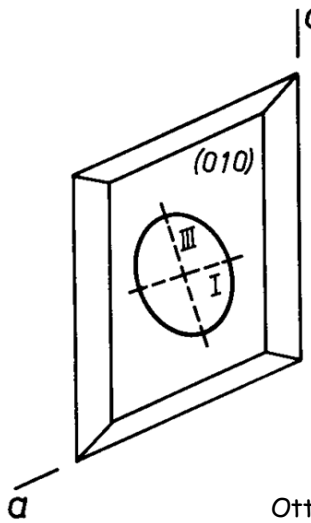
- Ferromagnetic materials can be magnetised more easily in some direction than in others → easy direction



Anisotropy in thermal properties

- Thermal expansion coefficient
- Thermal conductivity
  - ✓ Gypsum ($CaSO_4\,2H_2O$)





Thermal conductivity in direction III > that in direction I

→ ellipsoidal rather than circular

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Coupled effects – Pyroelectricity & Piezoelectricity

- Pyroelectricity – appearance of electrical potential difference across the solid when the material is heated
- Piezoelectricity - appearance of electrical potential difference in response to mechanical pressure on the material
- Magnitude & direction of the potential difference varies according to the direction of heat flow or the pressure

Anisotropy vs. Isotropy

- Anisotropy (이방성)
  - ✓ different values of a physical property in different directions
  - ✓ variation of a physical property with direction
  - ✓ Tensor
- Isotropy (등방성)
  - ✓ same value of a physical property in all directions
- In general, most solids are anisotropic with respect to some physical parameters, but isotropic to others
  - ✓ ex) solid NaCl is optically isotropic but mechanically anisotropic
- What feature of the structure of the solid state give rise to anisotropy? → **internal structure** of crystals

Characteristics of solid state

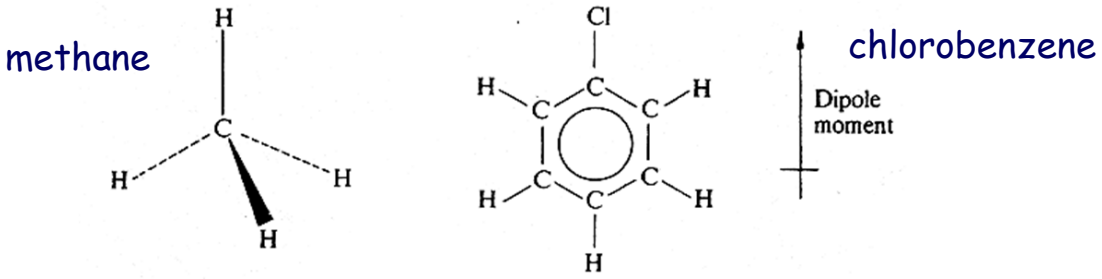
- High density
- Fixed size & shape
- Resistance to shear stress

&

- Anisotropy (Crystal)

- All gases are isotropic in all their physical properties
- Most liquids are isotropic

- What feature of the structure of the solid state will give rise to anisotropy?



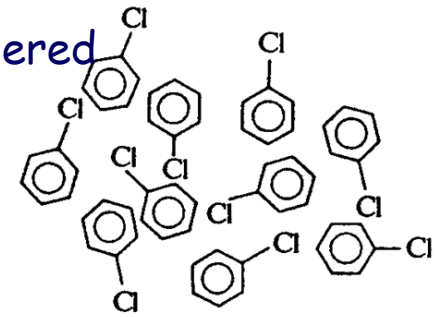
Molecular structure can give rise to anisotropy

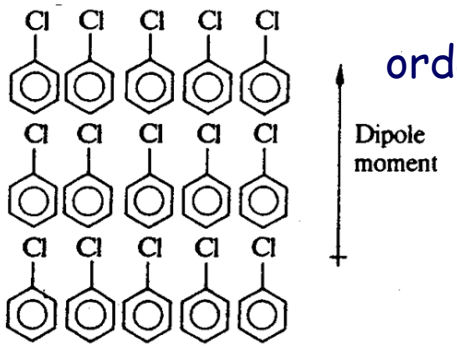
Variations in chemical structure can give rise to directional properties

Chlorobenzene molecules packed together in 2 different ways

Which of these structures is anisotropic?

disordered





ordered

A random array

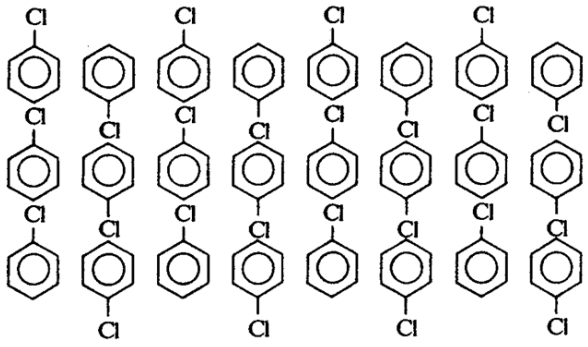
No net dipole moment in any direction → isotropic dielectric constant

A regular array

a net dipole moment → macroscopic anisotropy → anisotropic w.r.t. dielectric constant

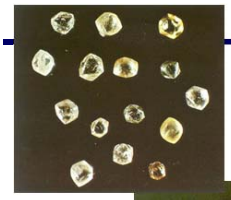
- Definite, well-defined, ordered array → directional properties
- Anisotropy is only possible when the molecules are arranged with regularity and order

Array of chlorobenzene molecules which is ordered but which has no net diple moment

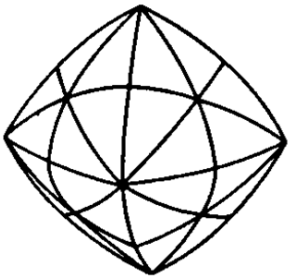


- Dipole moments cancel in pairs → dipole moment = zero in all directions
- Ordered, but no anisotropy.
- Isotropic with respect to its dielectric constant

- It is <u>not correct</u> to say that all ordered arrays will be anisotropic
- But it is undoubtedly true to say the converse, namely, that all anisotropic materials have an ordered structure



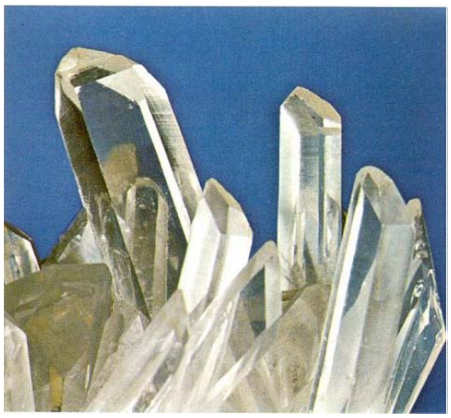
Diamond (C)

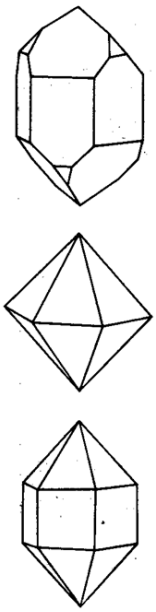


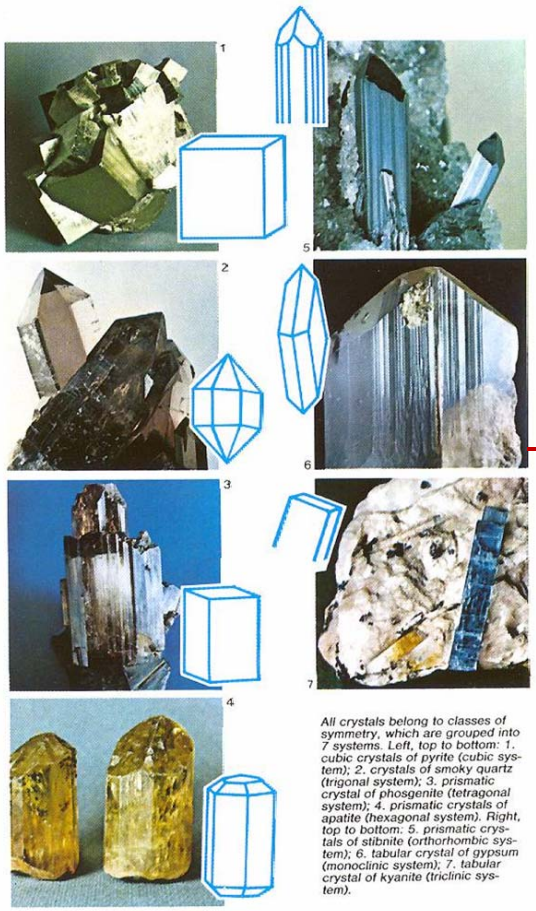
Cubic, Octahedron

Quartz (SiO2)

Hexagonal, Prismatic





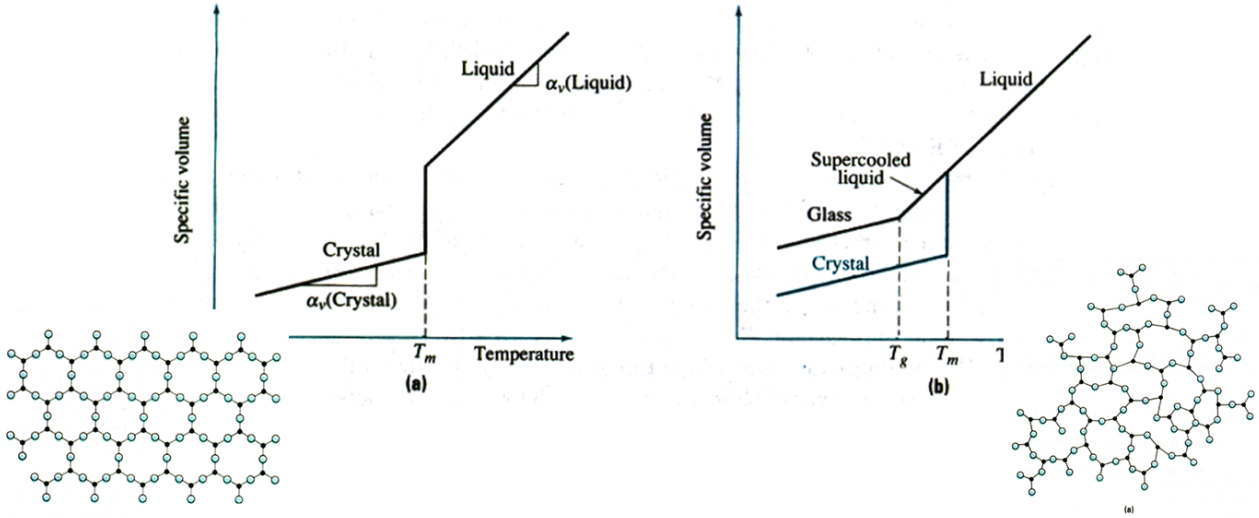


All crystals belong to classes of symmetry, which are grouped into 7 systems. Left, top to bottom: 1. cubic crystals of pyrite (cubic system); 2. crystals of smoky quartz (trigonal system); 3. prismatic crystal of phosgenite (tetragonal system); 4. prismatic crystals of apatite (hexagonal system). Right, top to bottom: 5. prismatic crystals of stibnite (orthorhombic system); 6. tabular crystal of gypsum (monoclinic system); 7. tabular crystal of kyanite (triclinic system).

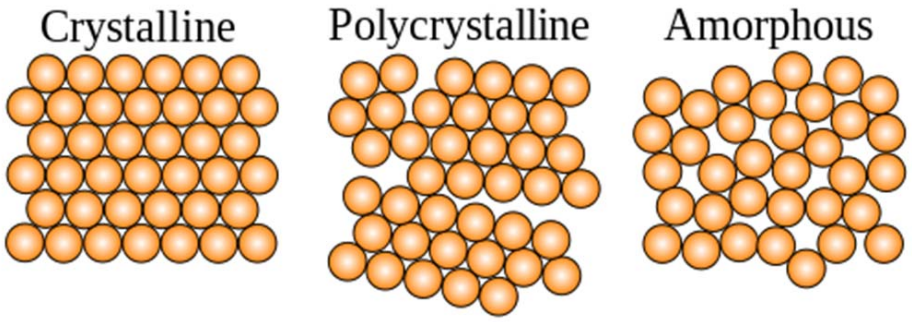
Simon & Schuster's Guide to Gems and Precious Stones

Are all solids crystalline? NO

- Crystal – solids with long-range, three-dimensional molecular order
  - ✓ Regular geometric shape
- Solids which are not crystals – amorphous (non-crystalline)
  - ✓ Glasses – do not have regular three-dimensional structure, do not have a sharp melting point → not crystalline



Crystalline, polycrystalline & amorphous



- Microscopically, a single crystal has atoms in a near-perfect periodic arrangement; a polycrystal is composed of many microscopic crystals (called "**crystallites**" or "**grains**"); and an amorphous solid (such as glass) has no periodic arrangement even microscopically.
- Example: quartz (crystalline SiO_2) vs fused silica (amorphous SiO_2)

- Perfect crystal vs. Crystals with defects
- X-ray diffraction
  - ✓ X-ray; a form of electromagnetic radiation with a wavelength comparable to the molecular spacing in a crystal
  - ✓ Diffraction; various phenomena which occur when a wave encounters an obstacle.
    - In classical physics, the diffraction phenomenon is described as the apparent bending of waves around small obstacles and the spreading out of waves past small openings.
    - As physical objects have wave-like properties, diffraction also occurs with matter and can be studied according to the principles of quantum mechanics.
    - Waves include sound, water, and electromagnetic waves such as visible light, X-rays and radio waves

todos

- Get the books
- Read before next class
  - ✓ Sherwood & Cooper Chapter 1 (1.7의 electron microscopy, AFM 부분 제외)
  - ✓ Ott Chapter 1, 2
  - ✓ Hammond Chapter 2
  - ✓ Krawitz 2.1, 2.2

Sherwood Chapter 1.9

- We do have means to focus X-ray.
- Focused X-ray can be as small as < 1um.